

## Supporting Information of

# Highly efficient hydrogenation of furfural to furfuryl alcohol over Cu-Al<sub>2</sub>O<sub>3</sub>-ZnO catalyst

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This supporting information contains Table S1 to S5, Fig. S1 to S3 and the specific experimental data.

**Table S1** Physical properties of CAZ<sub>x/2.0</sub>-200 catalysts.

| Sample                      | S <sub>BET</sub><br>(m <sup>2</sup> /g) <sup>a</sup> | V <sub>micro</sub><br>(cc/g) <sup>b</sup> | V <sub>meso</sub><br>(cc/g) <sup>c</sup> | S <sub>ext</sub><br>(m <sup>2</sup> /g) <sup>d</sup> | S <sub>micro</sub><br>(m <sup>2</sup> /g) <sup>e</sup> | d <sub>pore</sub><br>(nm) <sup>f</sup> |
|-----------------------------|------------------------------------------------------|-------------------------------------------|------------------------------------------|------------------------------------------------------|--------------------------------------------------------|----------------------------------------|
| CAZ <sub>0.5/2.0</sub> -200 | 168.21                                               | 0.065                                     | 0.140                                    | 48.23                                                | 119.98                                                 | 1.98                                   |
| CAZ <sub>1.0/2.0</sub> -200 | 121.13                                               | 0.062                                     | 0.104                                    | 31.91                                                | 89.21                                                  | 2.04                                   |
| CAZ <sub>1.5/2.0</sub> -200 | 39.69                                                | 0.032                                     | 0.074                                    | 19.27                                                | 20.43                                                  | 3.46                                   |
| CAZ <sub>2.0/2.0</sub> -200 | 16.47                                                | 0.020                                     | 0.071                                    | 16.47                                                | 0                                                      | 7.56                                   |
| CAZ <sub>2.5/2.0</sub> -200 | 9.17                                                 | 0.017                                     | 0.047                                    | 9.17                                                 | 0                                                      | 8.86                                   |

<sup>a</sup> S<sub>BET</sub>: Brunauer-Emmett-Teller (BET) method for calculating specific surface area;

<sup>b</sup> V<sub>micro</sub>: Micropore volume, calculated by t-plot method;

<sup>c</sup> V<sub>meso</sub>: Mesopore volume, calculated by the BJH method;

<sup>d</sup> S<sub>ext</sub>: t-plot method for calculating external specific surface area;

<sup>e</sup> S<sub>micro</sub>: t-plot method for calculating internal specific surface area.

<sup>f</sup> d<sub>pore</sub>: average pore radius at a single point (area is BET specific surface area):

**Table S2** Percentage composition of all elements of EDS elemental mappings in catalysts.

| catalysts                   | Percentage composition of all elements (%) |       |      |       |
|-----------------------------|--------------------------------------------|-------|------|-------|
|                             | Cu                                         | Al    | Zn   | O     |
| CAZ <sub>1.0/2.0</sub> -200 | 50.66                                      | 22.93 | 4.79 | 21.62 |
| CAZ <sub>1.5/2.0</sub> -200 | 68.19                                      | 13.34 | 4.66 | 13.81 |
| CAZ <sub>2.0/2.0</sub> -200 | 79.94                                      | 5.50  | 4.16 | 10.40 |

**Table S3** XPS atomic ratios (Cu/Al/Zn) for CAZ<sub>x/2.0</sub>-200.

| Entry | Catalysts                 | Cu    | Al    | Zn   |
|-------|---------------------------|-------|-------|------|
| 1     | CAZ <sub>1.0/2</sub> -200 | 3.92  | 93.65 | 2.43 |
| 2     | CAZ <sub>1.5/2</sub> -200 | 12.19 | 83.68 | 4.13 |
| 3     | CAZ <sub>2.0/2</sub> -200 | 14.58 | 81.39 | 4.03 |

**Table S4** Desorption amount in NH<sub>3</sub>-TPD for CAZ<sub>x/2.0</sub>-M.

| CAZ <sub>1.0/2.0</sub> -100 |        |                   |                                      |
|-----------------------------|--------|-------------------|--------------------------------------|
| Temperature at Maximum      |        |                   |                                      |
| Peak Number                 | (°C)   | Quantity (mmol/g) | Peak Active Gas Flow Rate (mmol/min) |
| 1                           | 131.72 | 0.09160           | 7.18E-04                             |
| 2                           | 337.76 | 0.49584           | 2.71E-03                             |
| 3                           | 485.29 | 0.80271           | 4.98E-03                             |
| CAZ <sub>1.5/2.0</sub> -100 |        |                   |                                      |
| Temperature at Maximum      |        |                   |                                      |
| Peak Number                 | (°C)   | Quantity (mmol/g) | Peak Active Gas Flow Rate (mmol/min) |
| 1                           | 113.01 | 0.13726           | 1.3047E-04                           |
| 2                           | 326.52 | 1.15620           | 3.8959E-03                           |
| CAZ <sub>1.5/2.0</sub> -200 |        |                   |                                      |
| Temperature at Maximum      |        |                   |                                      |
| Peak Number                 | (°C)   | Quantity (mmol/g) | Peak Active Gas Flow Rate (mmol/min) |
| 1                           | 114.37 | 0.15377           | 1.4128E-03                           |
| 2                           | 285.51 | 0.21903           | 2.5799E-03                           |
| 3                           | 347.39 | 0.64297           | 2.7318E-03                           |
| CAZ <sub>1.5/2.0</sub> -300 |        |                   |                                      |
| Temperature at Maximum      |        |                   |                                      |
| Peak Number                 | (°C)   | Quantity (mmol/g) | Peak Active Gas Flow Rate (mmol/min) |
| 1                           | 117.76 | 0.09273           | 7.6074E-04                           |
| 2                           | 276.26 | 0.90707           | 2.8635E-03                           |
| CAZ <sub>2.0/2.0</sub> -200 |        |                   |                                      |
| Temperature at Maximum      |        |                   |                                      |
| Peak Number                 | (°C)   | Quantity (mmol/g) | Peak Active Gas Flow Rate (mmol/min) |
| 1                           | 101.70 | 0.06193           | 6.4277E-04                           |
| 2                           | 286.99 | 0.56774           | 3.1106E-03                           |

**Table S5** Total acid number of the CAZ<sub>1.5/2.0</sub>-200 sample in the Py-IR test.

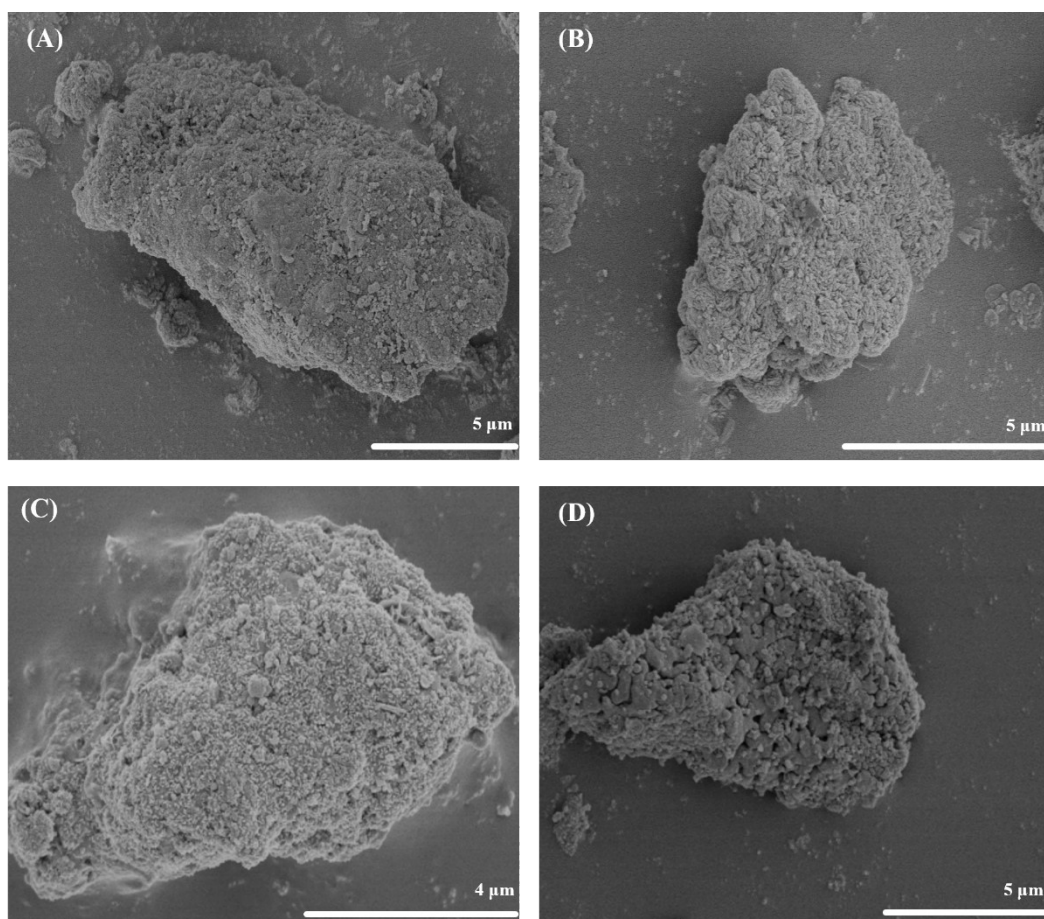
| Temperatue<br>(°C) | W<br>(mg) | Bronsted acid<br>area | Lewis<br>acid<br>area | Bronsted acid<br>content (umol/g) | Lewis acid<br>content<br>(umol/g) | total acid<br>content<br>(umol/g) | B/L     |
|--------------------|-----------|-----------------------|-----------------------|-----------------------------------|-----------------------------------|-----------------------------------|---------|
| 150                | 19.6      | 0.062                 | 0.97                  | 2.5126                            | 29.6914                           | 32.204                            | 0.08462 |
| 200                | 19.6      | 0.046                 | 0.76                  | 1.8642                            | 23.2634                           | 25.1275                           | 0.08013 |
| 350                | 19.6      | 0.023                 | 0.337                 | 0.9321                            | 10.3155                           | 11.2476                           | 0.09036 |

**Table S6** Hydrogen desorption amount in H<sub>2</sub>-TPD of CAZ<sub>1.5/2.0</sub>-M.

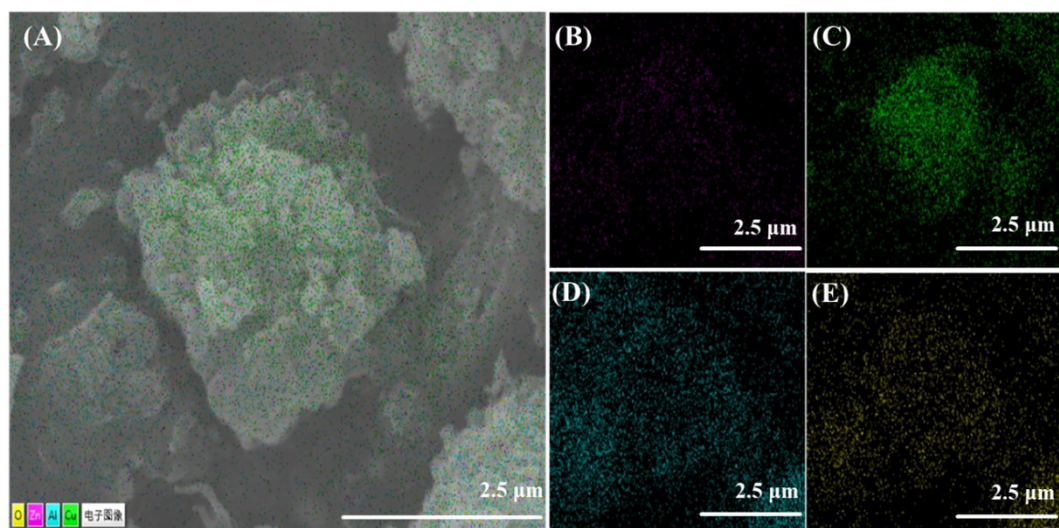
| CAZ <sub>1.5/2.0</sub> -100 |                                |                      |                                         |
|-----------------------------|--------------------------------|----------------------|-----------------------------------------|
| Peak<br>Number              | Temperature at Maximum<br>(°C) | Quantity<br>(mmol/g) | Peak Active Gas Flow Rate<br>(mmol/min) |
| 1                           | 271.90                         | 0.15538              | 4.8153E-04                              |
| CAZ <sub>1.5/2.0</sub> -200 |                                |                      |                                         |
| Peak<br>Number              | Temperature at Maximum<br>(°C) | Quantity<br>(mmol/g) | Peak Active Gas Flow Rate<br>(mmol/min) |
| 1                           | 91.91                          | 0.04428              | 3.8438E-04                              |
| 2                           | 280.80                         | 0.23572              | 7.8369E-04                              |
| CAZ <sub>1.5/2.0</sub> -300 |                                |                      |                                         |
| Peak<br>Number              | Temperature at Maximum<br>(°C) | Quantity<br>(mmol/g) | Peak Active Gas Flow Rate<br>(mmol/min) |
| 1                           | 88.13                          | 0.07481              | 5.2232E-04                              |
| 2                           | 349.13                         | 0.21098              | 6.2346E-04                              |

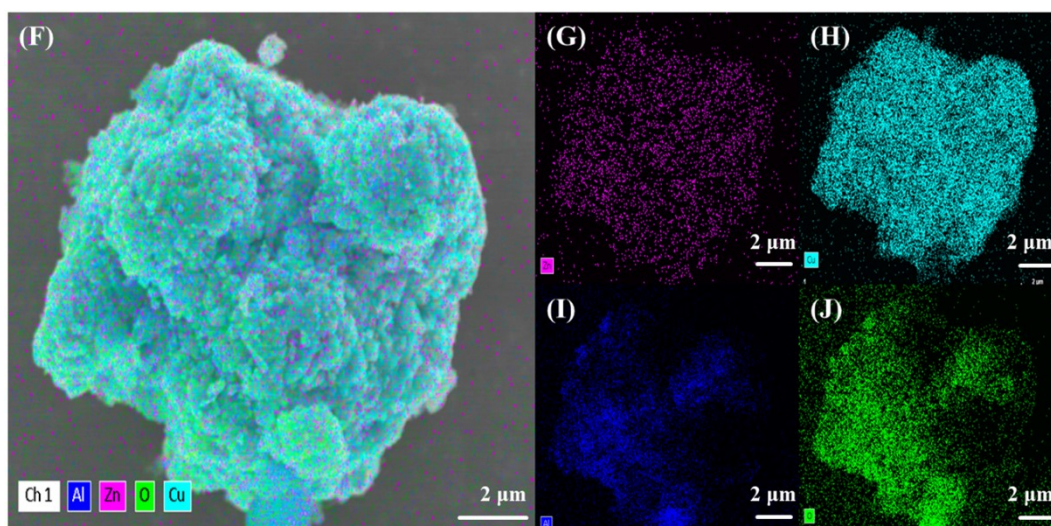
**Table S7** Actual bulk atom ratio of Cu<sup>0</sup>/Cu<sup>2+</sup>/Cu<sup>+</sup> measured by Cu XAES of the 35%Cu/Al<sub>2</sub>O<sub>3</sub> and 1.33%ZnO/35%Cu/Al<sub>2</sub>O<sub>3</sub> catalysts.

| Entry | Catalysts                                     | Cu <sup>0</sup> | Cu <sup>2+</sup> | Cu <sup>+</sup> |
|-------|-----------------------------------------------|-----------------|------------------|-----------------|
| 1     | 35%Cu/Al <sub>2</sub> O <sub>3</sub>          | 7.21            | 40.81            | 51.98           |
| 2     | 1.33%ZnO/35%Cu/Al <sub>2</sub> O <sub>3</sub> | 10.93           | 36.19            | 52.88           |

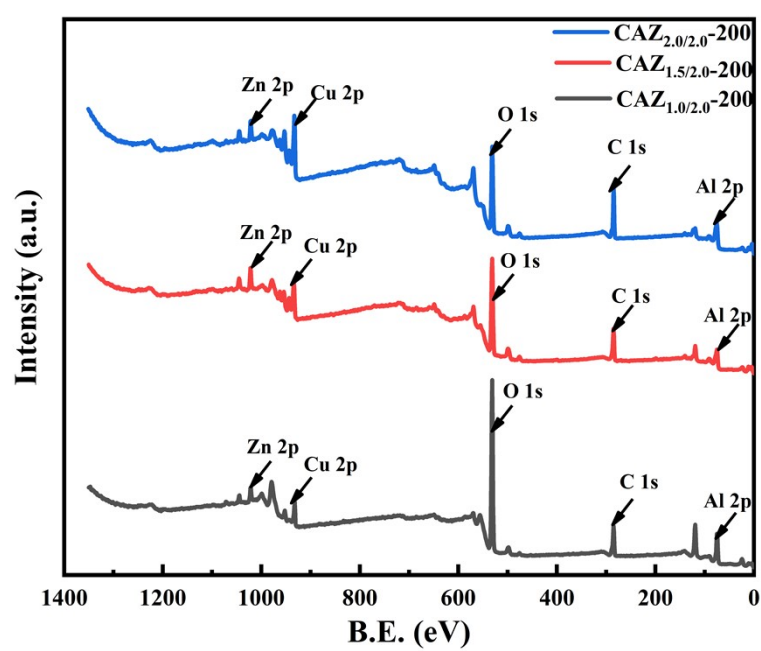


**Fig. S1** SEM images of samples (A) CAZ<sub>0.5/2.0</sub>-200, (B) CAZ<sub>1.0/2.0</sub>-200, (C) CAZ<sub>2.0/2.0</sub>-200, (D) CAZ<sub>2.5/2.0</sub>-200.





**Fig. S2** (A-E) EDS elemental mappings of the  $\text{CAZ}_{1.0/2.0}\text{-200}$  catalyst; (F-J) EDS elemental mappings of the  $\text{CA}_{2.0/2.0}\text{-200}$  catalyst.



**Fig. S3** XPS full spectrum of  $\text{CAZ}_{x/2.0}\text{-200}$  catalysts.

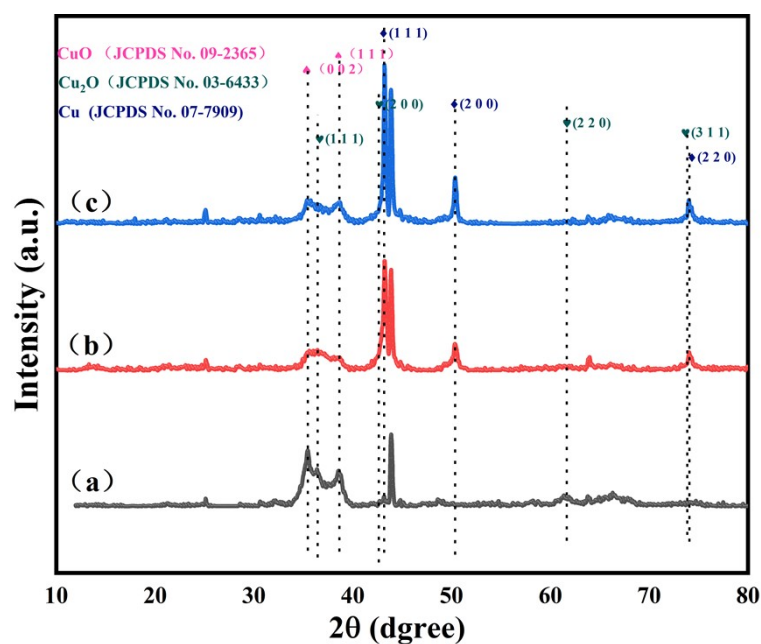


Fig. S4 XRD patterns of (a) CAZ<sub>15/2.0</sub>-100, (b) CAZ<sub>1.5/2.0</sub>-200 and (c) CAZ<sub>1.5/2.0</sub>-300.

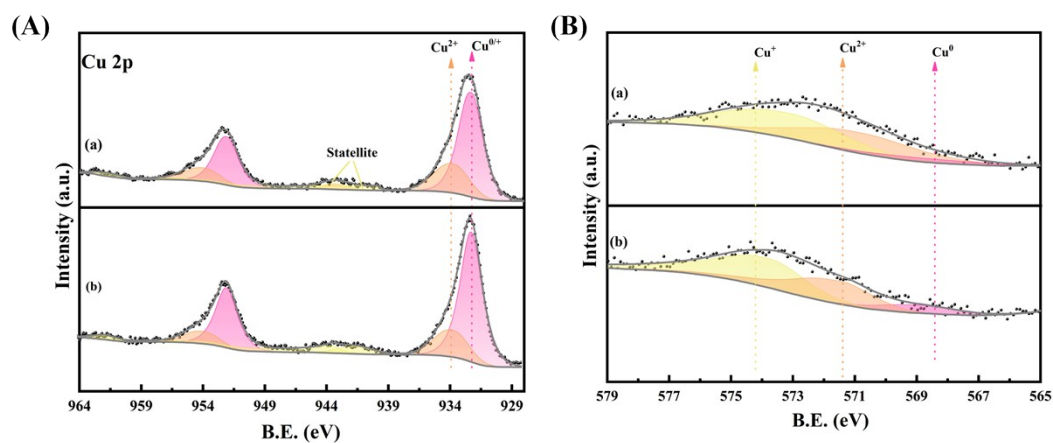


Fig. S5 (A) XPS spectra of the Cu 2p; (B) Corresponding XAES spectra of Cu LMM of (a) 35%Cu/Al<sub>2</sub>O<sub>3</sub> and (b) 1.33%ZnO/35%Cu/Al<sub>2</sub>O<sub>3</sub>.

The specific experimental data are shown in the tables below:

Three parallel tests per reaction.

The average FOL Yield (%)= average FAL conversion × average FOL selectivity

| FAL (1.20 g), catalyst (0.24 g), ethanol (60.0 g), 5 h. |                             |                    |                     |                       |
|---------------------------------------------------------|-----------------------------|--------------------|---------------------|-----------------------|
|                                                         |                             | FAL conversion (%) | FOL selectivity (%) | Average FOL Yield (%) |
| H <sub>2</sub> (1.5 MPa), 80 °C                         | CAZ <sub>0.5/2.0</sub> -200 | 63.39              | 99.79               |                       |
|                                                         | CAZ <sub>0.5/2.0</sub> -200 | 64.21              | 99.69               | 64.03                 |
|                                                         | CAZ <sub>0.5/2.0</sub> -200 | 65.06              | 99.65               |                       |
|                                                         | CAZ <sub>1.0/2.0</sub> -200 | 68.49              | 99.51               |                       |
|                                                         | CAZ <sub>1.0/2.0</sub> -200 | 69.21              | 99.20               | 68.26                 |
|                                                         | CAZ <sub>1.0/2.0</sub> -200 | 68.55              | 99.13               |                       |
|                                                         | CAZ <sub>1.5/2.0</sub> -200 | 98.66              | 99.57               |                       |
|                                                         | CAZ <sub>1.5/2.0</sub> -200 | 97.78              | 99.72               | 98.26                 |
|                                                         | CAZ <sub>1.5/2.0</sub> -200 | 99.27              | 99.78               |                       |
|                                                         | CAZ <sub>2.0/2.0</sub> -200 | 57.44              | 99.48               |                       |
|                                                         | CAZ <sub>2.0/2.0</sub> -200 | 58.15              | 99.67               | 57.96                 |
|                                                         | CAZ <sub>2.0/2.0</sub> -200 | 59.07              | 99.50               |                       |
|                                                         | CAZ <sub>2.5/2.0</sub> -200 | 45.76              | 99.13               |                       |
|                                                         | CAZ <sub>2.5/2.0</sub> -200 | 45.89              | 99.30               | 45.02                 |
|                                                         | CAZ <sub>2.5/2.0</sub> -200 | 44.40              | 99.38               |                       |
| N <sub>2</sub> (1.5 MPa), 80 °C                         | CAZ <sub>1.5/2.0</sub> -200 | 0.49               | 0                   |                       |
|                                                         | CAZ <sub>1.5/2.0</sub> -200 | 0.43               | 0                   | 0.00                  |
|                                                         | CAZ <sub>1.5/2.0</sub> -200 | 0.43               | 0                   |                       |

| FAL (1.20 g), catalyst (0.24 g), ethanol (60.0 g), 5 h, H <sub>2</sub> (1.5 MPa), 80 °C. |                    |                     |                       |
|------------------------------------------------------------------------------------------|--------------------|---------------------|-----------------------|
|                                                                                          | FAL conversion (%) | FOL selectivity (%) | Average FOL Yield (%) |
| CAZ <sub>1.5/2.0</sub> -100                                                              | 28.89              | 98.73               |                       |
| CAZ <sub>1.5/2.0</sub> -100                                                              | 29.38              | 99.12               | 28.60                 |
| CAZ <sub>1.5/2.0</sub> -100                                                              | 28.43              | 99.00               |                       |
| CAZ <sub>1.5/2.0</sub> -200                                                              | 98.66              | 99.57               |                       |
| CAZ <sub>1.5/2.0</sub> -200                                                              | 97.78              | 99.72               | 98.26                 |
| CAZ <sub>1.5/2.0</sub> -200                                                              | 99.27              | 99.78               |                       |
| CAZ <sub>1.5/2.0</sub> -300                                                              | 76.78              | 98.82               |                       |
| CAZ <sub>1.5/2.0</sub> -300                                                              | 75.83              | 98.98               | 75.20                 |
| CAZ <sub>1.5/2.0</sub> -300                                                              | 75.54              | 98.84               |                       |
| CAZ <sub>1.5/2.0</sub> -0                                                                | 19.39              | 98.54               |                       |
| CAZ <sub>1.5/2.0</sub> -0                                                                | 19.87              | 98.67               | 19.41                 |
| CAZ <sub>1.5/2.0</sub> -0                                                                | 19.72              | 99.04               |                       |

| FAL (1.20 g), catalyst (0.24 g), ethanol (60.0 g), 5 h, H <sub>2</sub> (1.5 MPa), 80 °C. |                    |                     |                       |
|------------------------------------------------------------------------------------------|--------------------|---------------------|-----------------------|
|                                                                                          | FAL conversion (%) | FOL selectivity (%) | Average FOL Yield (%) |
| 25%Cu/Al <sub>2</sub> O <sub>3</sub>                                                     | 5.88               | 87.87               | 5.35                  |
| 25%Cu/Al <sub>2</sub> O <sub>3</sub>                                                     | 6.07               | 88.12               |                       |
| 25%Cu/Al <sub>2</sub> O <sub>3</sub>                                                     | 6.26               | 88.43               |                       |
| 35%Cu/Al <sub>2</sub> O <sub>3</sub>                                                     | 18.24              | 92.79               | 17.12                 |
| 35%Cu/Al <sub>2</sub> O <sub>3</sub>                                                     | 18.35              | 93.44               |                       |
| 35%Cu/Al <sub>2</sub> O <sub>3</sub>                                                     | 18.5               | 93.52               |                       |
| 45%Cu/Al <sub>2</sub> O <sub>3</sub>                                                     | 15.03              | 97.65               | 14.62                 |
| 45%Cu/Al <sub>2</sub> O <sub>3</sub>                                                     | 14.99              | 97.96               |                       |
| 45%Cu/Al <sub>2</sub> O <sub>3</sub>                                                     | 14.86              | 97.61               |                       |
| 1.33%ZnO/35%Cu/Al <sub>2</sub> O <sub>3</sub>                                            | 24.03              | 95.38               | 23.08                 |
| 1.33%ZnO/35%Cu/Al <sub>2</sub> O <sub>3</sub>                                            | 24.52              | 95.64               |                       |
| 1.33%ZnO/35%Cu/Al <sub>2</sub> O <sub>3</sub>                                            | 23.99              | 95.39               |                       |

| FAL (1.20 g), catalyst (0.24 g), ethanol (60.0 g), 1.5 MPa H <sub>2</sub> , 5 h  |                    |                             |
|----------------------------------------------------------------------------------|--------------------|-----------------------------|
| Temperature (°C)                                                                 | FAL Conversion (%) | Average FOL Selectivity (%) |
| 70                                                                               | 32.97              | 99.49                       |
| 70                                                                               | 33.45              | 99.64                       |
| 70                                                                               | 33.69              | 99.58                       |
| 75                                                                               | 57.49              | 99.52                       |
| 75                                                                               | 57.72              | 99.69                       |
| 75                                                                               | 57.53              | 99.74                       |
| 80                                                                               | 98.66              | 99.57                       |
| 80                                                                               | 97.78              | 99.72                       |
| 80                                                                               | 99.27              | 99.78                       |
| 85                                                                               | 100                | 99.79                       |
| 85                                                                               | 100                | 99.71                       |
| 85                                                                               | 100                | 99.75                       |
| FAL (1.20 g), catalyst (0.24 g), ethanol (60.0 g), 85 °C, 1.5 MPa H <sub>2</sub> |                    |                             |
| Reaction time (h)                                                                | FAL Conversion (%) | Average FOL Selectivity (%) |
| 1                                                                                | 18.87              | 100                         |
| 1                                                                                | 18.44              | 100                         |
| 1                                                                                | 17.80              | 100                         |
| 2                                                                                | 79.88              | 99.92                       |
| 2                                                                                | 80.34              | 99.96                       |
| 2                                                                                | 81.31              | 99.94                       |
| 3                                                                                | 99.16              | 99.8                        |
| 3                                                                                | 99.00              | 99.87                       |
| 3                                                                                | 99.14              | 99.85                       |
| 4                                                                                | 99.32              | 99.73                       |
| 4                                                                                | 99.44              | 99.89                       |
| 4                                                                                | 99.71              | 99.81                       |
| 5                                                                                | 100                | 99.79                       |
| 5                                                                                | 100                | 99.71                       |
| 5                                                                                | 100                | 99.75                       |

| FAL (1.20 g), catalyst (0.24 g), ethanol (60.0 g), 85 °C, 4 h |                    |                             |
|---------------------------------------------------------------|--------------------|-----------------------------|
| H <sub>2</sub> Pressure (MPa)                                 | FAL Conversion (%) | Average FOL Selectivity (%) |
| 0.5                                                           | 15.95              | 100                         |
| 0.5                                                           | 16.83              | 100                         |
| 0.5                                                           | 16.36              | 100                         |
| 1.0                                                           | 57.98              | 99.69                       |
| 1.0                                                           | 59.43              | 99.78                       |
| 1.0                                                           | 58.81              | 99.78                       |
| 1.5                                                           | 99.32              | 99.73                       |
| 1.5                                                           | 99.44              | 99.89                       |
| 1.5                                                           | 99.71              | 99.81                       |

| FAL (1.20 g), catalyst (0.24 g), ethanol (60.0 g), 85 °C, 1.5 MPa H <sub>2</sub> , 2 h |                    |                             |
|----------------------------------------------------------------------------------------|--------------------|-----------------------------|
| Test runs                                                                              | FAL Conversion (%) | Average FOL Selectivity (%) |
| 1                                                                                      | 79.88              | 99.92                       |
| 1                                                                                      | 80.34              | 99.96                       |
| 1                                                                                      | 81.31              | 99.94                       |
| 2                                                                                      | 78.30              | 99.41                       |
| 2                                                                                      | 79.14              | 99.53                       |
| 2                                                                                      | 77.61              | 99.41                       |
| 3                                                                                      | 77.69              | 96.97                       |
| 3                                                                                      | 77.76              | 96.88                       |
| 3                                                                                      | 77.71              | 96.88                       |
| 4                                                                                      | 75.43              | 96.53                       |
| 4                                                                                      | 75.63              | 96.67                       |
| 4                                                                                      | 75.71              | 96.60                       |
| 5                                                                                      | 72.12              | 96.23                       |
| 5                                                                                      | 72.38              | 96.12                       |
| 5                                                                                      | 72.25              | 96.10                       |